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Volatile organic compound emissions from an engine fueled with an ethanol-biodiesel-diesel blend

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ABSTRACT

With the advent of energy crisis, vehicle engines need alternative energy sources eagerly to supply power. Ethanol-biodiesel-diesel blends are considered to be effective solutions. One way is diesel engines burning blended fuels. Diesel engines exhaust many kinds of volatile organic compounds (VOCs) when mixed fuels burn in them. Extremely poisonous as these VOCs are, they can cause severe damage to the natural environment as well as human health. To explore the characteristics of the unregulated emissions produced by diesel engines and then to limit them, research and studies should be conducted. The research in this paper used a single-cylinder diesel engine and a chromatograph mass spectrometer to investigate 9 kinds of VOCs (benzene, toluene, n-butyl acetate, ethylbenzene, p-xylene, m-xylene, styrene, o-xylene, n-undecane) emissions of ethanol-biodiesel-diesel (EBD) and diesel (D). The solid phase adsorption-thermal desorption-gas chromatography mass spectrometry (GC/MS) had an advantage in measuring and analyzing VOC emissions, so it was used for investigating the total emissions of 9 kinds of VOCs. Based on the standard curves of VOCs, the GC/MS computed the peak area of each VOC and realized the quantitative analysis of target compounds. By the calculating equation of VOC specific emissions and other test parameters (exhaust flow, engine power, dilution ratio, test time), the test got VOC specific emissions of two different fuels under different operating conditions. The test selected five typical conditions to collect exhaust when burning EBD and D. EBD contained 10 vol. % ethanol, 30 vol. % biodiesel, 55 vol. % diesel, 2.5 vol. % n-butyl alcohol and 2.5 vol. % iso-octyl alcohol, which had strong stabilities and good economy. From the analysis of the test results of VOC emissions, it was found that EBD increased total emissions by 84.2% at rated power but decreased by 14.85% at 10% load and by 20.39% at 50% load compared with diesel. But under other test conditions, VOC emissions with EBD were lower than diesel. VOC emissions of the two fuels were mainly benzene and toluene at medium and high load, which increased up to 47.4%. Emissions of other components increased at low load. In general, it was possible to decrease VOC emissions at medium or low loads when the diesel engine was fueled with EBD. The ozone specific reactivities (SR) of the engine exhaust for the two test fuels were approximately the same for the selected operating conditions. The SRs of EBD were a bit lower than D at medium and low loads. EBD had an advantage relative to VOC emissions which was found mainly at medium and low loads. This study is valuable for contributing to the building of a VOC emissions standard and for demonstrating the potential benefit of substitute fuels in reducing VOCs.

1. Introduction

Volatile organic compounds (VOCs) defined by the World Health Organization are kinds of organic compounds that have atmospheric pressure boiling points ranging from 50 °C to 260 °C [1,2]. VOCs are identified in more than 300 different chemical structures that include aldehydes, ketones, alkanes, aromatic hydrocarbons, alkenes and halogenated hydrocarbons [3,4]. VOCs discharged by engines are mainly

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derived from the unburnt or partially burnt fuel and the evaporation of various fuel additives and lubricants [5–8]. Most of VOCs have a strong toxicity, which maybe cause great harm to the natural environment and human health [9–12].

Vehicle exhaust is the main source of VOCs in cities [13,14]. A. K. H. Lau [15] monitored the VOC concentrations in the ambient air in HK and found that Vehicle emissions were one of the most significant VOC sources. S. G. Brown [16] found that 22%–24% of the VOCs in the air of the Los Angeles basin originated from Vehicle emissions. Y. Song [17] concluded that vehicle emissions contributed 52% to the total ambient VOCs in Beijing.

In the last two decades, several studies have focused on the VOCs emitted from gasoline engine, including emission factors [18,19]. There have been few studies of the VOCs of diesel vehicles because of the lower emission factors of diesel engines compared with gasoline engines. However, in China, the diesel vehicle population has continued to grow because of the improved market acceptance of diesel technology due to its low fuel consumption, strong power and good durability [20]. Therefore, the VOC emissions from the exhaust of diesel engines can't be ignored.

To control VOC emissions of vehicles, China has formulated *Determination of Volatile Organic Compounds and Carbonyl Compounds in Cabin of Vehicles* for the vehicle now [21,22]. *The determination* is applied to detect air pollution caused by the component materials and decoration materials in the vehicle cabin under static conditions, but it does not take the running vehicle exhaust into consideration [21,23]. This paper mainly focuses on VOC emissions when the diesel engine is burning ethanol-biodiesel-diesel blended fuel by referring to *the determination* that is about the measurement types and methods of VOCs, and provides a reference for further restricting and monitoring vehicle emissions.

2. Research theory

According to the definition of Lars Molhave [24,25], VOC emissions can be measured by canister adsorption-gas chromatography mass spectrometry, solid phase adsorption-solvent extraction-gas chromatography mass spectrometry and solid phase adsorption-thermal desorption-gas chromatography mass spectrometry.

This experiment adopts the solid phase adsorption-thermal desorption-gas chromatography mass spectrometry (GC/MS) for measuring and analyzing VOCs emissions from a S195 diesel engine. The advantages of GC/MS are measurement automation, without the use of harmful toxic reagents, convenient storage and transport of collection tubes, and low concentration pollutant measurement [26]. According to the standard method TO–17 of the environmental protection agency (EPA) [27], the sampling tubes should be filled with Tenax TA adsorbent to capture VOCs in the samples. Tenax TA is a kind of porous polymer that is made up of 2, 6 − diphenyl on benzene ether, and it is especially suitable for adsorption enrichment of volatile and semi-volatile organic compounds in gas purging samples containing water regardless of the water content.

Suggested by the US Environmental Protection Administration Institute of Standard Sample [27], The standard sample used for the test was the standard solution which contained 9 kinds of VOCs, including benzene, toluene, n-butyl acetate, ethylbenzene, p-xylene, m-xylene, styrene, o-xylene and n-undecane, and their concentration all being 10μg/ml. Fig. 1 shows the reference material for the total ion chromatogram. Under the same conditions, the same kinds of VOC components have the same retention time. Because the retention time of p-xylene and m-xylene are the same, they can be combined to analysis. By comparing the peak retention time of each unknown component in the collected sample with the reference, it is possible to qualitatively analyse the sample and identify the components' chemical name. Because the sampling inevitably included some instrument error with each measurement, some deviation in the retention time was accommodated.

The test made use of the peak area external standard method for the quantitative analysis of VOCs [24]. First, the test extracted standard solution 1, 2, 4, 10, 20, 40 μl with the help of trace samplers. Then the test injected standard solution into Tenax TA sampling tube through the flowing carrier gas by using the standard gas preparation device produced by USA Marks Company. Finally, the test used GC/MS to analyze the Tenax TA sampling tube which contained standard solution after the secondary thermal analysis. The content (ug) of VOCs target compounds specified as the abscissa and the peak area after deducting the blank response set as the vertical axis were used to draw the standard curve. Fig. 2 shows a toluene standard curve of the testing. Other compounds were similar to this standard curve.

Table 1 lists curve equations, correlation coefficients and relative standard deviation (RSD) for the 9 VOCs. According to the standard curve, it realizes the quantitative analysis of target compounds by returning peak area of each component in collect sample. Through the

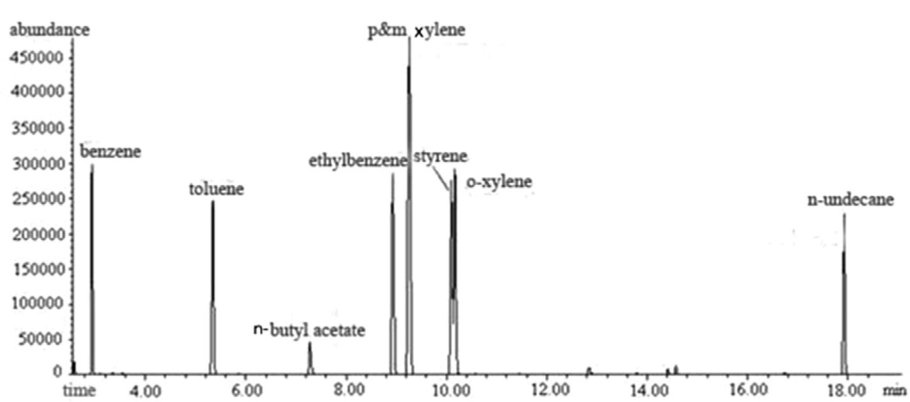

Fig. 1. Reference material of total ion chromatogram.

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